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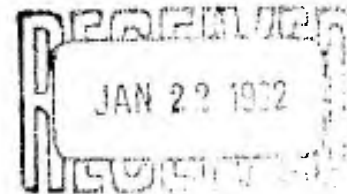
Textile Functional Finishes Report No. 195

PYROLYSIS OF A COTTON/NYLON FABRIC

by

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## Table of Contents

Abstract	<u>Page</u> iii
Introduction	1
Description of Equipment	
A. Sample Cell	2
B. Chromatography Unit	2
C. Cold Traps	2
Procedure	3
Analysis of Pyrolysis Products	
A. Fraction A	3,6
B. Fraction B	6,8
C. Fraction C	8
D. Fraction D	8
Mechanism of Pyrolysis	9

### ABSTRACT

The research involved in this work constitutes an examination of the gases evolved by organic solids as they are exposed to thermal radiation. Gas chromatography has been utilized as a tool for analyzing the products evolved from an untreated 50% cotton, 50% nylon 66 fabric which was exposed to radiation derived from a carbon arc. The products were carried via helium gas through a dry ice - acetone trap into an adsorption chromatograph and subsequently analyzed. The condensate in the dry ice - acetone trap was analyzed on a Resoflex R-296 column, while the tarry substance on the cell window and fritted glass filter was identified utilizing infrared. A third fraction, collected in liquid nitrogen, was also analyzed by infrared techniques. The products characterized were CO, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, several polar organic components, and levoglucosan.

It was found that the pyrolysis of cotton/nylon produced greater quantities of CO<sub>2</sub> and N<sub>2</sub> than were observed in the pyrolysis of cotton. In addition, many aliphatic amines were detected in the products evolved from the cotton/nylon fabric.

## I. INTRODUCTION

Gas chromatography has become an ever increasingly powerful tool in studying products of complex gas phase reactions. This method supplies a rapid and accurate determination regardless of the organic solid. A chromatography unit together with an infrared spectrometer or a mass spectrograph provides one with the necessary tools for the analysis of many liquid and gas mixtures. Recently, polymers and copolymers have been analyzed with this technique by identification of their pyrolysis<sup>1</sup> products.

One such application of gas chromatography has been the determination of the degradation products of cellulosic materials. Recently, investigators at Arthur D. Little<sup>2</sup> analyzed the products evolved when cotton and fire retardant treated cotton were exposed to radiation from a carbon arc. No fundamental qualitative difference was observed in the pyrolysis mechanism as compared to that observed by prior investigators using longer pyrolysis times.<sup>3,4</sup>

In the carbon arc technique an organic solid is suspended in a helium carrier gas and exposed to intense thermal radiation emitted by a high current carbon arc. The vapors resulting from various conditions of pyrolysis are characterized by first separating the materials in a series of cold traps and analyzing each fraction by appropriate techniques.

In the present study the combined carbon arc - chromatography technique was applied to a fabric consisting of 50% cotton and 50% nylon. It has been observed in the laboratory that some blends of cotton with nylon require more energy for ignition than do equivalent weight all cotton fabrics. Consequently, it was desired to know if the superior behavior of the cotton/nylon blend could, in part, be attributed to the composition of its pyrolysis products.

The fabric studied in this work was cloth, cotton/nylon (50/50) 9 oz/sq yd, OG 107. The weight change after dyeing was approximately 5-8%. The dye itself was a mixture of four dyestuffs, namely, Olive-T-#69525 molecular formula  $C_{45}H_{61}O_5N_2$ , Olive Green-B-#69505  $C_{29}H_{40}O_3N$ ; Vat Yellow 2 #67300-1  $C_{28}H_{38}O_2N_2S_2$  and Khaki 2H #71050  $C_{70}H_{98}O_8N_4$ . The dyestuff mixture was composed of 7.9 oz/gal Olive T, 1/2 oz/gal Olive Green B, 3.8 oz/gal of Khaki 2G, and 2.4 oz/gal Vat Yellow.

## II. DESCRIPTION OF EQUIPMENT

### A. Sample Cell

A glass cell equivalent to that described by Barnes<sup>5</sup> was used to contain the sample of fabric during each exposure. In essence, the cell consisted of a glass cylinder with a ground glass neck at one end and a flat window at the opposite end. Inlet and exit ports were provided for connecting to the helium flow lines. A ground glass insert, with solid base into which were inserted three needles, completed the assembly. In practice, a disc of fabric was affixed to the needles and inserted into the cell for exposure to the radiation.

### B. Chromatography Unit

The chromatography unit consisted of a thermal conductivity cell (TELL#9193-Gls/mac), associated heating coils, controls, and a Minneapolis-Honeywell recorder. The adsorption columns were fabricated from six to eight foot lengths of stainless steel tubing into which were packed the required adsorbents, i.e., silica gel, activated charcoal, and resoflex.

The resolution of each chromatogram partially depends upon the mixed vapors moving very quickly into the column. The vapors which are evolved from the irradiated organic solid can attenuate the thermal flux, therefore a flow rate of helium high enough to prevent accumulation of vapors in front of the target was maintained (50cc/min).

As the pyrolysis products are swept by the carrier gas into the chromatographic column they are selectively adsorbed and subsequently eluted at different intervals depending upon their retention time. Each has a characteristic adsorption on a given column, and its elution time distinguishes it from other gases. The subsequent passage of an eluted gas through the thermal conductivity cell produces an imbalance in the circuit of the cell. The degree of imbalance is transmitted to the recorder and with time produces a history of the elution process. The graphical history is then used to identify the gas, and in many instances to determine the quantity evolved.

### C. Cold Traps

Two cold traps were utilized. One, a dry ice - acetone trap, was positioned between the glass cell and the chromatography unit, and the second, a liquid nitrogen trap, was positioned in the exit line of the unit. The traps were utilized for collecting fractions and as a means of introducing samples into the infrared spectrophotometer. Each trap consists of a four-way twin V-bore, 2mm stopcock, and approximately 30



inches of 1/4-inch O.D. pyrex glass tubing. The tubing forms the inclosure of the trap and an inlet and outlet arm with 12/30 male ground glass joints are provided. The traps, patterned after that by Bazinit and Walsh,<sup>6</sup> are designed to provide turbulent flow along the length of the tubing and an excess of surface upon which the gas may condense.

### III. PROCEDURE

Samples of the fabric to be pyrolyzed were die cut and positioned within the glass cell parallel to the window and at the focal point of the high intensity carbon arc. Prior to pyrolyzing any samples the energy loss due to absorption of the window was determined by measurements made with a disc calorimeter. These measurements showed the cell losses to be 14.6% of the incident energy and indicate that the ultra-violet portion of the spectrum was essentially eliminated.

After placing the fabric sample in position within the cell, the system was permitted to stabilize with the carrier gas (helium) flowing through it. When using the cold traps as fraction collectors, they were first flushed with helium while being immersed in the appropriate coolant. The carrier gas was then allowed to by-pass the traps, through the four-way stopcocks, until the fraction was ready to be collected. After pyrolyzing a sample, the carrier stream continued to by-pass the traps until the recorder trace indicated that a component was being eluted. At this time the traps were opened and the fraction condensed.

In order to identify the gases evolved by the pyrolysis, the chromatography unit was first calibrated by introducing measured quantities of pure gases. This was accomplished by inserting a hypodermic syringe containing these gases into a rubber fitting in the intake line. After pyrolysis, the products were collected as fractions and analyzed. Fraction A consists of all gases not condensible at dry ice - acetone temperatures, Fraction B the components condensible at dry ice - acetone temperature, Fraction C is that group of components condensible at liquid nitrogen temperature, and Fraction D, products condensible at 25°C. These latter products were collected within the sample cell and adjacent glass tubing.

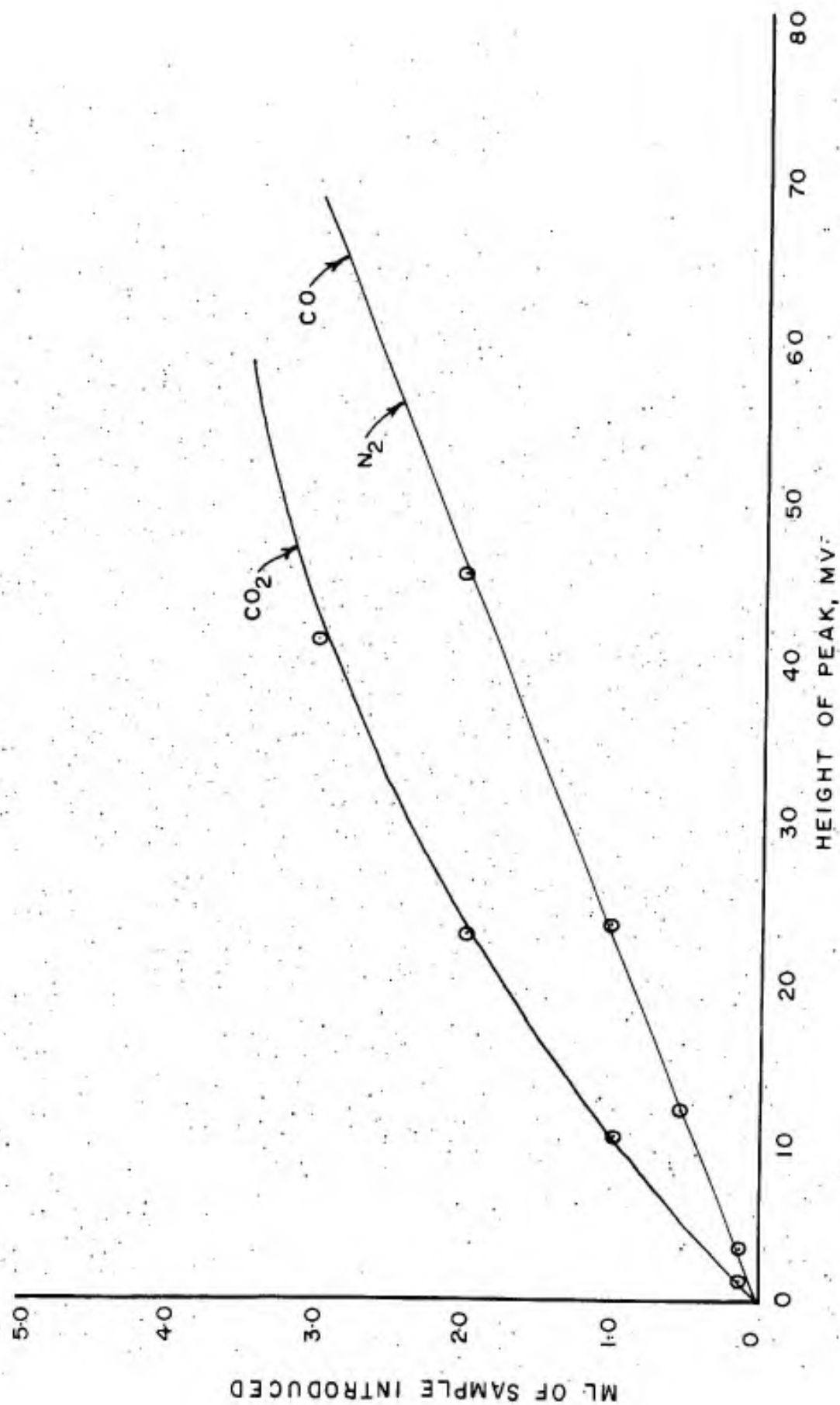
### IV. ANALYSIS OF PYROLYSIS PRODUCTS

#### A. Fraction A

Fraction A consists of many gases, each of which has a characteristic adsorption on a given column. Activated charcoal separates hydrogen, nitrogen, carbon monoxide, and methane, in that order, while silica gel separates carbon dioxide. Each column was first calibrated by introducing

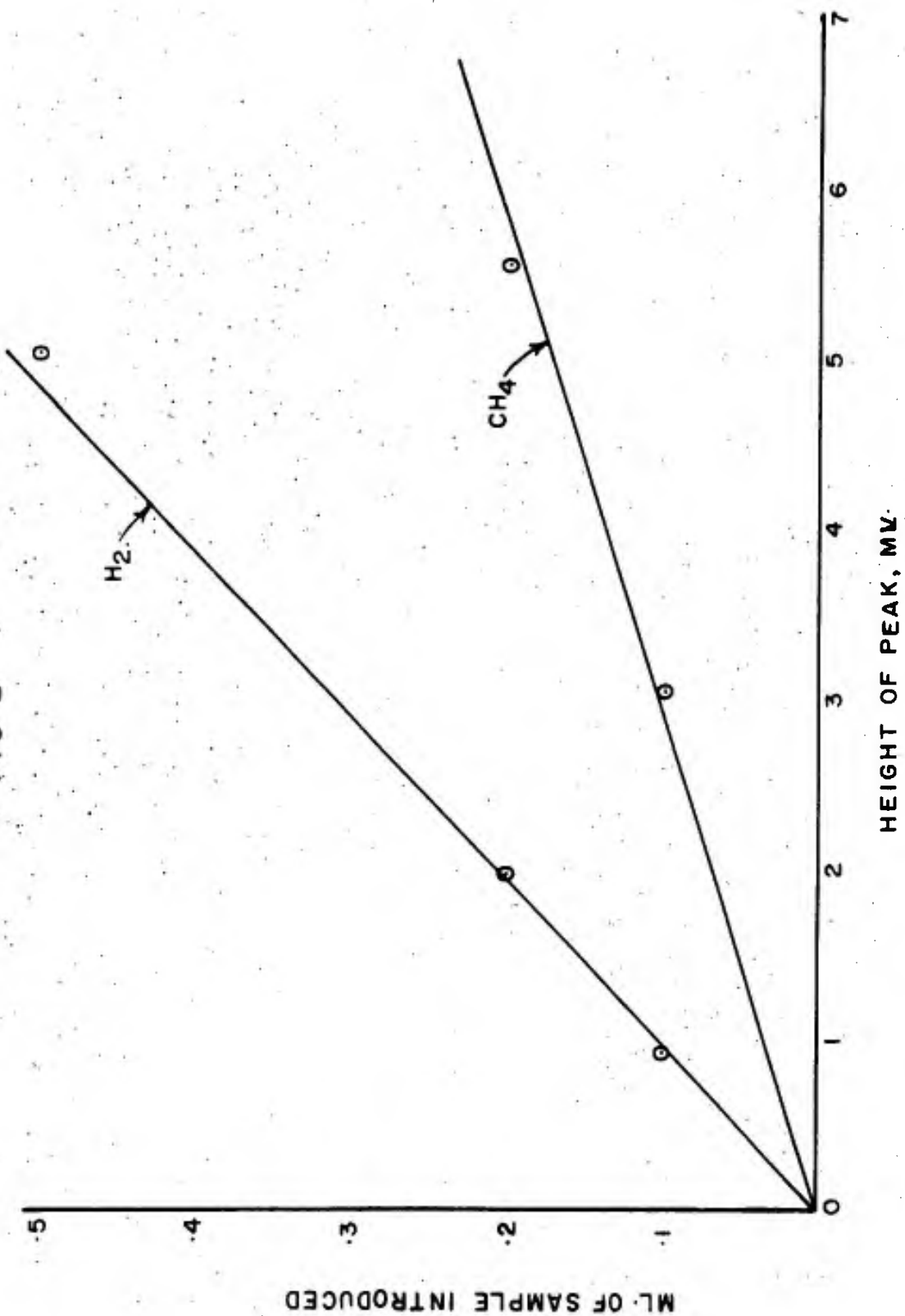
CO<sub>2</sub> ON SILICA GELL, N<sub>2</sub> ON ACTIVATED CHARCOAL,  
AND CO ON ACTIVATED CHARCOAL

FIG. 1



CALIBRATION CURVES FOR H<sub>2</sub> AND  
CH<sub>4</sub> ON ACTIVATED CHARCOAL

FIG. 2



a given quantity of a known gas and observing the height of the peak of the chromatograph and the elution time. A plot of quantity of sample introduced vs. height of peak yields a straight line which is subsequently used to analyze the quantity of the specific component in the pyrolysis products. Similarly, a plot of log of retention time vs. boiling point yields curves which can be used to identify a component. The calibration curves obtained in this manner are shown in Figures 1 and 2. Using these curves, the analysis of Fraction A was obtained and is shown in Table I.

TABLE I

Analysis of Fraction A

<u>Column</u>	<u>Gas</u>	<u>Elution Time (min)</u>	<u>Products (ml)</u>
Charcoal	H <sub>2</sub>	2	.27
	N <sub>2</sub>	4	2.30
	CO	6	3.05
	CH <sub>4</sub>	14	.115
Silica Gel	CO <sub>2</sub>	2	2.75

B. Fraction B

Fraction B is collected in dry ice - acetone at -80°, and is then reintroduced into the system with a Resoflex R-296 column as the new chromatograph. Each component is then eluted in accordance with its boiling point with the lower boiling components being eluted first. The Resoflex column was calibrated by passing through the column a group of known compounds that were suspected as being possible degradation products of the decomposition of nylon and cotton. The retention time of these compounds was again determined and a plot of log of elution time vs. boiling point is shown in Figure 3. From Figure 3 the components of Fraction B obtained by pyrolysis were identified. The results of the analysis of this fraction can be seen in Table II.

FIG-3  
CALIBRATION OF THE RESOFLEX COLUMN

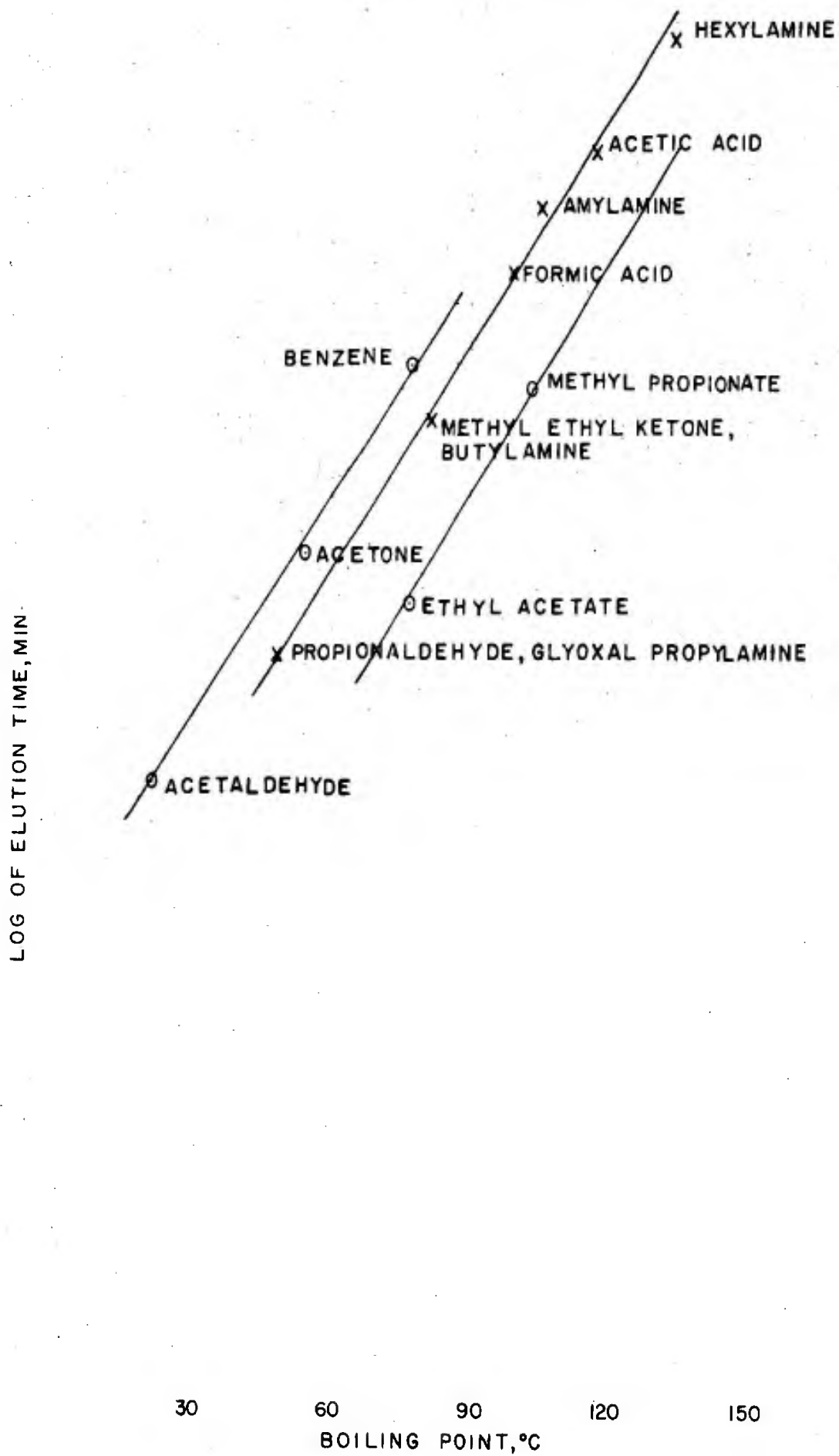


TABLE II

Analysis of the Pyrolysis Products of Fraction B

<u>Compound</u>	<u>Elution Time (min)</u>
acetaldehyde	.75
propionaldehyde, glyoxal, propylamine	1.0
acetone	1.5
methylethylketone, butylamine	2.0
formic acid	3.25
amylamine	4.0
acetic acid	5.0
hexylamine	7.0

Fraction B contained many polar organic compounds. This aqueous distillate readily reduced Benedict's and Fehling's solution, indicating the presence of the aldehyde group. It also restored the color to Schiff's reagent, also indicating positive aldehyde formation. This distillate also formed a precipitate with 2,4 dinitrophenylhydrazine, indicating the presence of the ketone group. The presence of amines was confirmed by a positive Hinsburg test. The pH of the condensate was 3-5.

C. Fraction C

Fraction C, the components condensible at liquid nitrogen temperature, consisted of carbon dioxide and methane. These components were collected in a gas bottle and transferred to a gas cell for infrared analysis. Bands for the former compound were observed at 2.75 and 4.4 u, while the latter one absorbs at 3.35, 6.5, and 7.7 u.

D. Fraction D

Fraction D was examined using infrared and was found to have absorption peaks at 3.2, 5.9, and 9.6 u. The band at 5.9 u denotes carbonyl content, whereas the other bands are characteristic of levoglucosan.

## V. MECHANISM OF PYROLYSIS

The pyrolysis mechanism of cotton cellulose has been postulated as being governed by the scission of the 1,4 glycosidic linkage. This rate-determining step is probably followed by a hydride shift to produce an intramolecular rearrangement yielding 1,6 anhydro $\alpha$ , $\beta$ -glucopyranose, commonly called levoglucosan, the main decomposition product of the pyrolysis.

An examination of the degradation products of the cotton/nylon fabric indicates a scission probably occurs in the nylon at the weaker C-N bond (48.6 K cal/mole) producing abnormally large quantities of nitrogen. The high percentage of carbon dioxide could result from a scission at the C-C bond (58.6 K cal/mole).

It was found that the pyrolysis of cotton/nylon produced a larger quantity of CO<sub>2</sub> than was observed in the pyrolysis of cotton. This, coupled with the large fraction of N<sub>2</sub> found in these products, would tend to suppress ignition of the cotton/nylon fabric. In addition, many aliphatic amines were detected in the products evolved from the cotton/nylon fabric.

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